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If fossil fuels continue to be a major part of the world's energy supply, effective means must be developed to deal with the carbon emissions. Geologic sequestration of supercritical CO_2 is expected to play a major role in mitigating this problem. Separating carbon dioxide from other gases is the most costly aspect of schemes for geologic sequestration. That cost is driven by the complexity and energy intensity of current chemical-stripping methods for separating carbon dioxide.

Our experience in water treatment technology indicated that an entirely new approach could be developed, taking advantage of water's propensity to separate gases that ionize in water (like CO_2) from those that do not (like N_2). Even though water-based systems might not have the extreme selectivity of chemicals like substituted amines used in industrial systems today, they have the potential to tolerate NO_x , SO_x , and particulates while also producing clean drinking water as a valuable byproduct. Lower capital cost, broader range of applicability, environmental friendliness, and revenue from a second product stream give this approach the potential to significantly expand the worldwide application of carbon separation for geologic sequestration.

Here we report results for separation of CO_2 from flue gas by two methods that simultaneously separate carbon dioxide and fresh water: ionic pumping of carbonate ions dissolved in water, and thermal distillation. The ion pumping method dramatically increases dissolved carbonate ion in solution and hence the overlying vapor pressure of CO_2 gas, allowing its removal as a pure gas. We have used two common water treatment methods to drive the ion pumping approach, reverse osmosis and electrodialysis to produce pure CO_2 . This novel approach to increasing the concentration of the extracted gas permits new approaches to treating flue gas, because the slightly basic water used as the extraction medium is impervious to trace acid gases that destroy existing solvents, and no pre-separation is necessary. Thermal distillation uses boiling water to steam strip solid sorbents – the steam is recovered as fresh water.

We anticipate that our method will compete favorably with current chemical stripping systems used for CO_2 separation at power plants, which incur a 35% energy penalty. Thus we expect to offer a dramatically improved solution for removing carbon from hydrocarbon combustion. Our method can be demonstrated on small sources, which will enable us to conduct the demonstrations required to build confidence in the method. If successful, we will be in a position to advance a follow-on proposal for a demonstration at the 10-MW scale.

Approach

A few major power plants around the world currently remove carbon dioxide from flue gas, for sale as an industrial product. Oil companies commonly remove carbon dioxide from natural gas to improve its energy content. In both cases the most common technology is a temperature-swing absorption (TSA) using a methylated

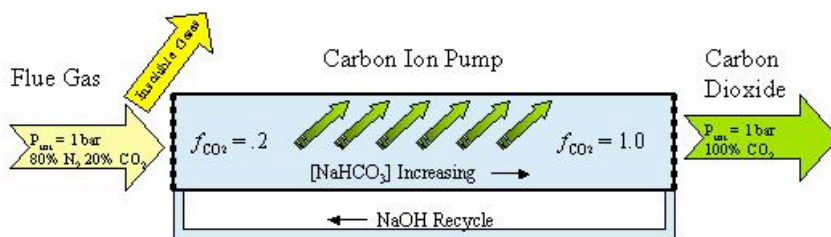


Figure 1. Ion pumping works by increasing the fugacity of CO_2 over the working fluid by increasing the concentration of carbonate

ethyl amine solvent (MEA). The flue gas contacts the MEA dissolved in water in a packed column, and then the carbonated solution is heated to 120°C to extract a nearly pure carbon dioxide gas. Sulfur and large amounts of nitrous oxide are removed ahead of this step because they bind so tightly to the solvent that they cannot be removed.

Instead of increasing the fugacity by physical means, we can also change it by chemical manipulation. For instance, adding acid to a solution will cause carbon dioxide to leave solution, but is not practical on a large scale. An alternative is to increase the concentration of the dissolved species in solution, which will result in a nearly linear increase in the gas pressure over the solution (of course there are nonlinearities, but when removing a neutral gas from an ionic solution, the “salting out” effect disproportionately favors gas evolution at higher concentration).

The ion concentration required for this approach is exactly what happens on the concentrate side of a water desalinization system. In reverse osmosis, electrodialysis, or thermal distillation there is always a “waste” half of the process where ions are concentrated. Our method takes advantage of this side of the process to generate carbon dioxide gas from the concentrated bicarbonate ions.

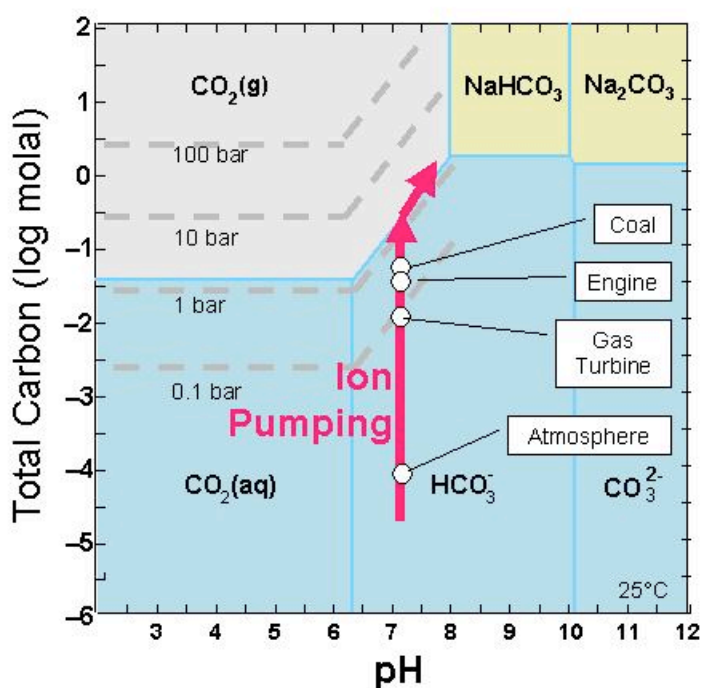


Figure 3. Increasing ionic strength at constant composition results in production of CO₂ gas.

The concentrate is recombined with the dilute stream and re-cycled to the water wash. Nitrate and sulfate will be concentrated with the bicarbonate and either removed separately as solids or



Figure 2. The combined thermal/reverse-osmosis water plant in Fujaira, UAE produces 450,000 m³ water/day and 500 MW electricity from 667 MW total.

We have modeled the effects of the ion pumping process for a simple sodium bicarbonate-phosphate water system. The ion pump effectively increases the concentration of bicarbonate (red line) with a corresponding increase in carbon dioxide pressure. We assume here that the carbon dioxide is released at a pressure of one bar. The ion pump increases the HCO₃⁻ concentration; for flue gas from a coal-fired power plant, an increase of 30 will release about 6.5 grams of pure carbon dioxide per liter of fluid.

At industrial scale we envision a process where the flue gas is first dissolved in slightly alkaline water. The water passes into the ion pump. The ion pump produces a concentrate from which carbon dioxide is released. Phosphate is included to buffer pH and increase CO₂ carrying capacity.

separated using known industrial processes such as solvent extraction or ion exchange.

Global Application – How Good Does It Have To Be To Make A Difference?

Having established the feasibility of the method, we have attempted to focus our efforts by determining

what the most critical aspects are for global-scale application. What performance must be achieved? What are the fundamental limiting factors? To understand this we can look at the typical operations of major power plants, and large-scale water treatment plants. To first order our process uses the same engineering and energy, so the costs will be very similar.

- Typical 500MW coal power plant = 1×10^6 ton C per year emission
- Fujairah water treatment plant (current largest) 164×10^9 l/yr produced @ 167MW cost.

The Fujairah value is useful because it tells us both the cost of processing water (in energy units), and the value of the water produced in the same units. Running a water plant of this kind to treat one coal-fired power plant's emissions would require that the treated water be carrying 1×10^{12} g C / 164×10^9 l water = 6.1g C/l. If all that water could be sold into a market like Fujairah's, the carbon treatment would be free.

However, it is unlikely that in actual operation all the water can be sold while the entire buffer salts are effectively recycled. The buffer salts will be mixed with whatever waste salts come in with the water to be treated, which will certainly require recycling of some of the water. Thus the critical factors for efficiency and cost become the overall carrying capacity of the buffered water, and the amount of the water recycled versus sold.

A compelling application of the method would be at non-coastal power plants where the separated CO_2 is planned to be sequestered in deep brine aquifers at more than 1000m depth below the plant. This brine would be used as the feedstock for the water treatment plant, which would create free space in the brine aquifer for storage of the CO_2 and disposal of salt from the water process. The required buffer salts will be mixed with whatever waste salts come in with the water to be treated. Thus the critical factors for efficiency and cost become the overall carrying capacity of the buffered water, and the amount of the buffer recycled versus replaced.

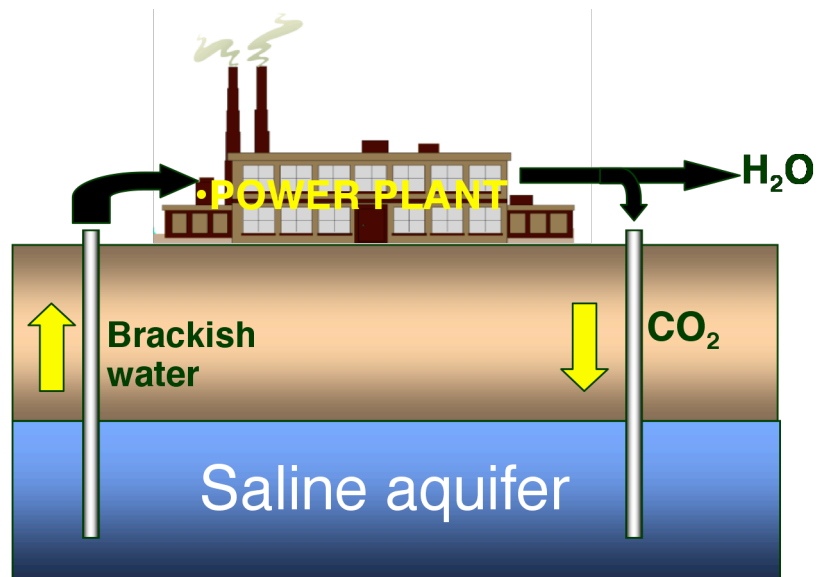


Figure 4. Schematic application of decarbonation/desalination to management of saline aquifers for carbon dioxide disposal.

Experimental Results

An advantage to our carbon dioxide separation approach is that any desalination technology can be used to carry out the separation. Initially, we used electrodialysis to demonstrate the initial proof of concept. Following that, we used reverse osmosis to carry out the separations. Both were successful but raised issues about buffer management. Calculations showed that the cost of separating dissolved buffers would be prohibitive. We therefore developed a system using solid, slurried buffers derived from ion exchange media. These work better with thermal distillation methods than with the ion pump. Either process may be advantageous for a particular separations need depending on the local availability and needs for brines, brackish waters, and fresh waters, and the compositions of those waters. With the development of new types of desalination technologies some additional potentially favorable options become available.

Results of the use of electrodialysis and reverse osmosis as the desalination methods are presented in Aines et al. 2006.

Electrodialysis and Reverse Osmosis

Some results of using electrodialysis to process a simulated flue gas having 12% CO₂ are shown below. Our first year's feasibility tests used 100% CO₂ as the gas source. The current results demonstrate that the method works at lower and more relevant CO₂ partial pressures. The plots show that as the electrodialysis unit is fed partially saturated CO₂ fluid, fluid on the concentrate side increases in total carbon because bicarbonate (HCO₃⁻) from the feed crosses the ED membrane into the concentrate. While this happens, the bulk salinity also increases as other salt components, in addition to bicarbonate, are enriched in the concentrate at the expense of the feed solution. Eventually, as this process continues, the partial pressure of CO₂ reaches one atmosphere and degassing begins (horizontal blue arrow).

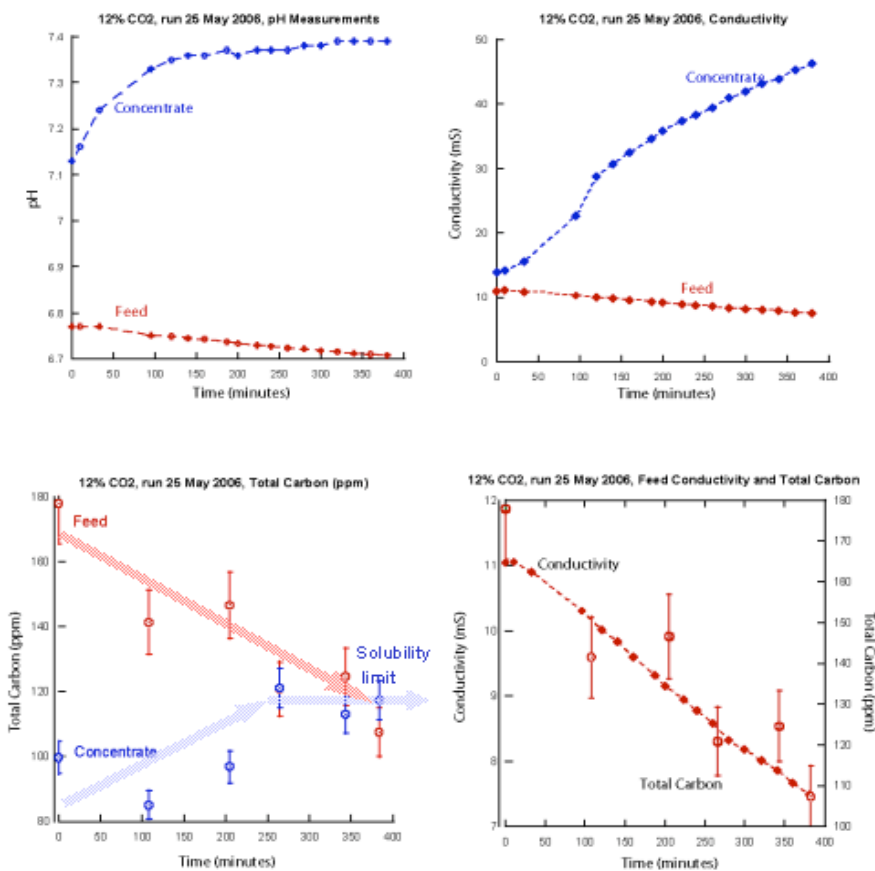


Figure 5. Results from test using electrodialysis to separate carbon dioxide from source having 12 mole % CO₂.

We carried out the same experiment (12% CO₂ source) using reverse osmosis and found that the CO₂ crossed the membrane and effervesced on the permeate side. We also observed a much lower pH for the permeate relative to the concentrate, due to CO₂ transport (known to take place during reverse osmosis desalination). It was unclear at the start of these tests whether the CO₂ would build up in the concentrate and degas as bubbles, or travel through the membrane into the

permeate and degas from the permeate, as observed in our tests. Relative rates of CO₂ transport vs. overall process conditions would appear to control where the CO₂ ends up. Because we were not able to capture representative gas samples from either stream (permeate or concentrate) with our initial test procedure, we decided to investigate better gas sampling and analysis methods before carrying out additional RO tests.

Thermal Desalination

Apparatus. For this study a mockup of a thermal desalination process was used (Figure 6). 230 g of ion exchange media was placed in a 500 ml round bottom flask which was then filled to 400 ml total volume using either distilled water or artificial sea water. The system was charged with CO₂ by bubbling gas into the round bottom flask for fixed periods of time. This was an inefficient charging system but provided good repeatability so that accurate measurements of total CO₂ absorption and water production could be made. The vessel was attached to a vertical condenser by an offset joint that allowed the condensate to drain into a separate vessel for measurement of the distilled water produced. The condenser separated steam from carbon dioxide produced during heating. The carbon dioxide left the top of the condenser and was conducted to a sealed 2.5 l flask filled with water. As the gas entered this vessel it displaced the water, which overflowed into a graduated cylinder providing a precise measurement of the volume of gas produced.

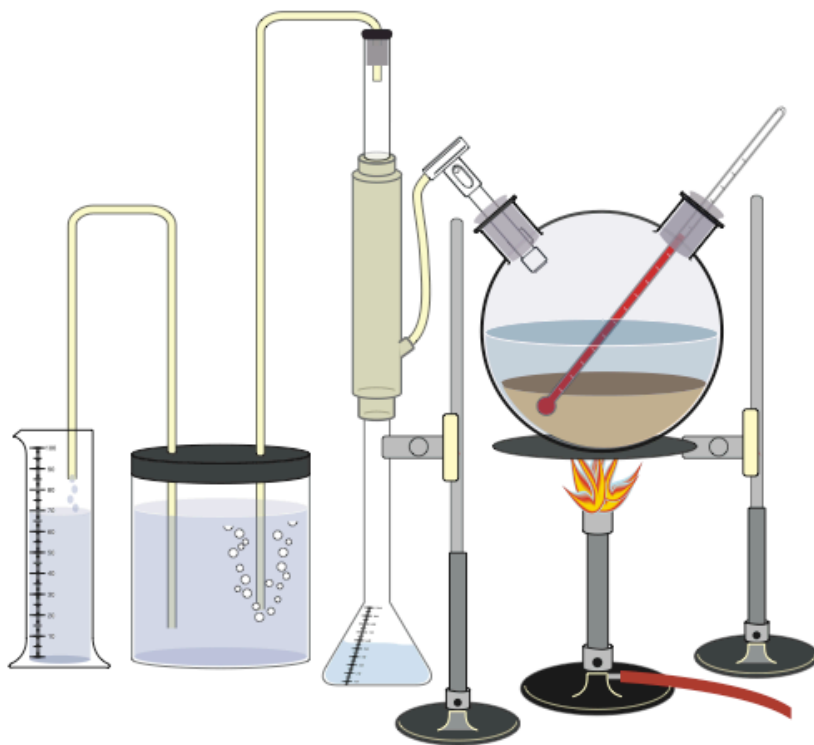


Figure 6. Gas is evolved during heating and passes through a cold-water condenser which removes steam. The condensed water is measured as the amount of produced fresh water. The dried gas then passes to a closed container where it displaces water, which flows into a graduated cylinder for measurement of the volume of gas produced.

The blank for the system consisted of the amount of noncondensable gas in the system (air) prior to heating – this gas was displaced by steam. This blank gas is present in the headspace of the boiling flask and in the tubing and condenser. Blanks were measured by repeatedly heating the

uncharged system until significant water accumulated below the condenser, indicating that the system was filled with steam. Figure 2 shows displacement-temperature curves for those blanks. Each run took approximately 1500 seconds to complete. Most test runs were begun at a system temperature of 50°C – two runs in Figure 2 are shown starting at 22°C. An exponential fit to the blank data was used to correct test data. Data for runs started at >50°C proved more suitable for this blank correction method.

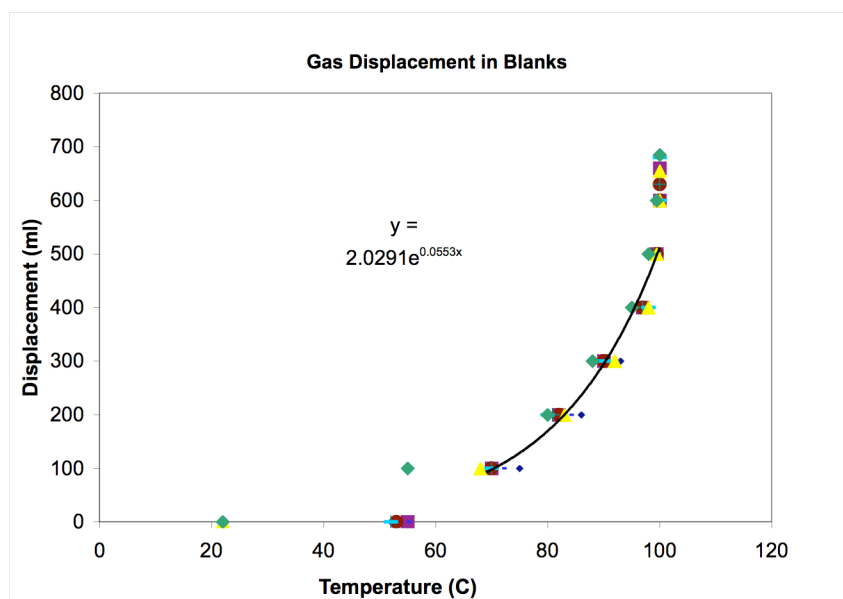


Figure 7. Gas displacement in eight blank runs (uncharged system) as a function of temperature. The black line shows the exponential fit to the runs begun at > 50°C.

Materials. The ion exchange media was obtained from Purolite Corporation. Two types were used: A847 (a gel type weak base anion exchange resin with tertiary ammonium functional groups) and A850 (a gel type strong base anion exchange resin with quaternary ammonium functional groups).

Table 1. Ion Exchange Resins Tested. Data in this report are from tests using A850.

Property	A 847	A850
Polymer Matrix Structure	Crosslinked Gel Acrylic	Crosslinked Gel Acrylic
Functional Groups	Tertiary Ammonium	Quaternary Ammonium
Specific Gravity Moist Cl ⁻ form	1.08	1.08 g/l
Total Ion Exchange Capacity Cl ⁻ form	1.6 eq/l (min)	1.25 eq/l (min)
Maximum CO ₂ loading	1.47 mmole/g	1.15 mmole/g or 0.051 g CO ₂ /g

Only preliminary testing was conducted with A847. The data reported here are only for A850. The two resins behaved similarly but we did not attempt a quantitative comparison. At maximum loading of the A850 resin we would anticipate a maximum of 0.051 g CO₂ per gram of resin, or 11.7 g in the 230 grams of resin used in the experiment. This is based on the buffering ability of the resin assuming one mole of CO₂ converts to one mole of HCO₃⁻ requiring one mole of buffer capacity. Water used in testing was either low conductivity deionized water, or a synthetic seawater reconstituted from dried sea salt (intended for aquarium use). We confirmed the density of the reconstituted seawater but did not conduct any chemical analysis. Carbon dioxide used to charge the samples was purchased as premixed laboratory gas from a commercial vendor. Pure CO₂, and mixtures of 19%, 5%, and 1% CO₂ in N₂ were used.

Results. Experiments were begun using pure CO₂ in deionized water to evaluate the total capacity of the bead/water system. The primary focus is on total loading capacity and the amount of heat and time required to discharge the beads. Typical results for the charging and discharge of the beads are shown in Figure 8. Figure 9 shows the amount of water produced, and Figure 10 demonstrates that the results are very similar when seawater is used instead of tap water. Figure 11 summarizes the total loading observed as a function of the initial CO₂ concentration and the loading time.

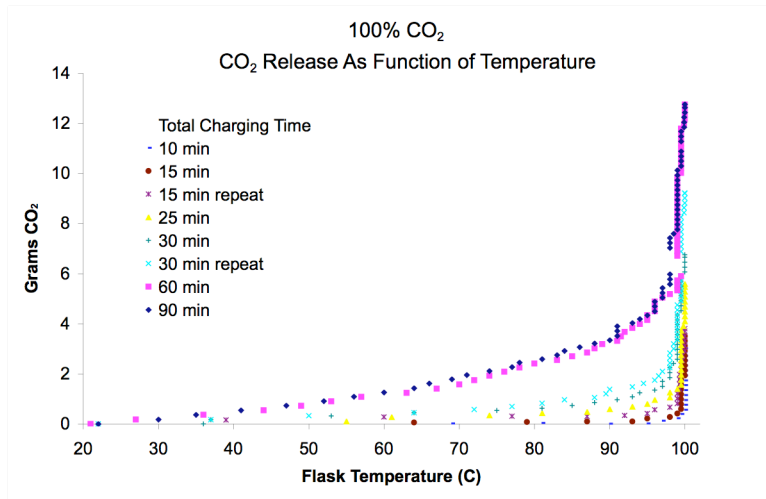


Figure 8. Rate of release of CO₂ from A847 media charged with pure CO₂.

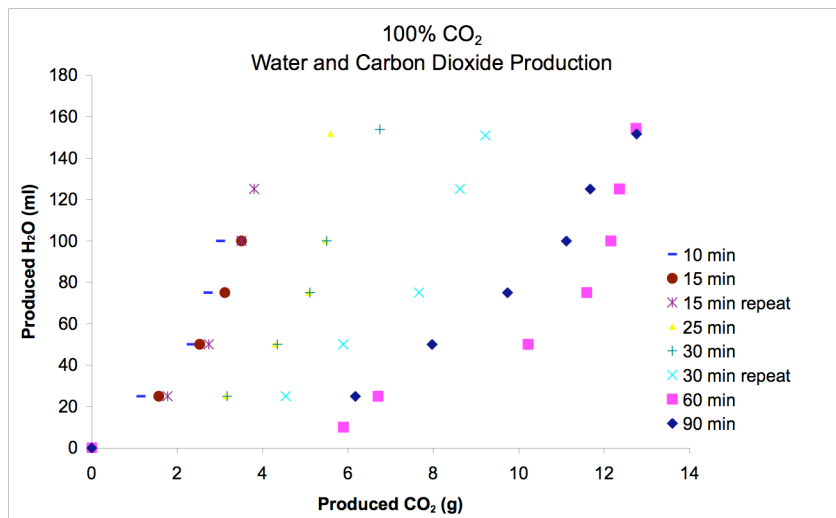


Figure 9. Water production as a function of CO₂ produced.

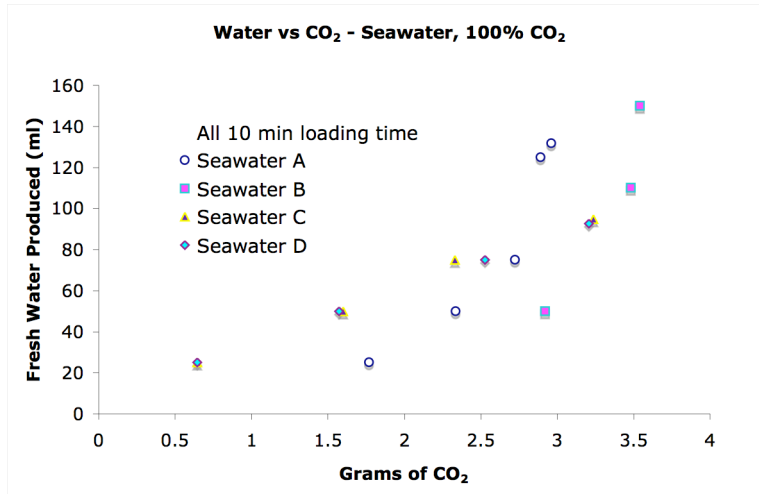


Figure 10. Fresh water and carbon dioxide production using seawater is indistinguishable from production using deionized water (compare Figure 9- 10 min loading time).

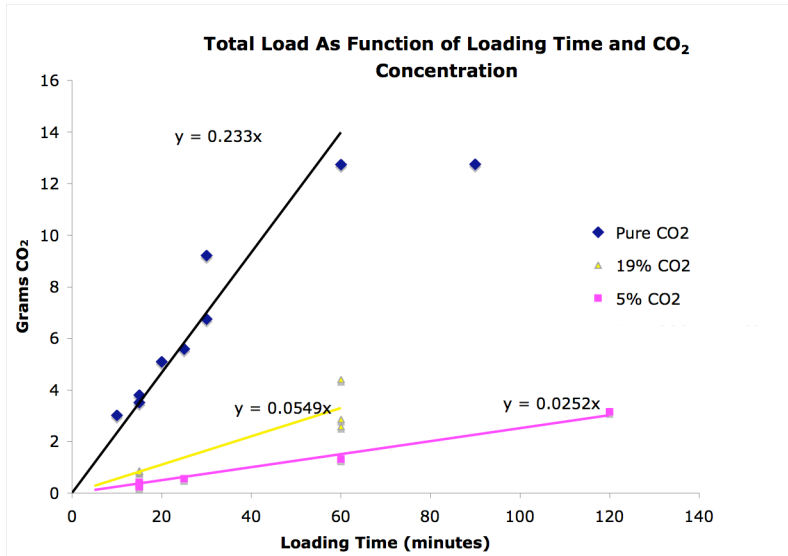


Figure 11. Variation in total loading caused by the initial concentration of CO₂ in the charging gas.

Table 2. Observed loading rates as a function of CO₂ concentration in the feed gas.

CO ₂ Concentration	Observed Loading Slope Grams/Minute	Expected Loading Slope From Concentration Ratio	Rate Increase Relative to 100%
100%	.233	.233	
19%	.0549	.0443	124%
5%	.0252	.0116	217%

Discussion of Thermal Desalination

The majority of the experiments in the thermal part of this study were conducted with tap water. Figure 10 shows that production from seawater is indistinguishable from tap water production. Thus this method could be used to desalinate seawater, and probably other saline waters.

The rate of absorption of CO₂ onto the resin will be a function of the concentration of CO₂ in the loading gas, and the length of time allotted for absorption. Table 2 shows that at lower concentrations, the loading rate is higher than the ratio of CO₂ concentrations. This is beneficial for the overall process, but the mechanism for that improvement is not known.

The desorption process will be controlled by both the temperature of the resin and the concentration of CO₂ in the gas outside the resin. When the host water is boiling, the gas phase outside the resin has effectively zero CO₂. In principal the energy demand for stripping CO₂ could be calculated from experiments like ours by calculating the excess of energy required to generate steam (as produced water, Figure 9). Unfortunately our energy input was not calibrated, so we cannot calculate that value. However, the enthalpy of absorption of CO₂ into amine liquids is on the order of 2 kJ/g CO₂. From Figure 9 we see that for the fully loaded resin, about 13 g of steam are produced for every g of CO₂. Producing 13 g of steam requires roughly 13 x 2.4 kJ = 31 kJ, dwarfing any heat required to liberate the CO₂ from the amine in the ion exchange resin. Thus the energy for this process is primarily used for creating fresh water, with the ancillary benefit of releasing the CO₂ from the ion exchange media.

A key parameter in this method is the total loading of carbon dioxide carried in the feed water. This study demonstrated that with conventional ion exchange media we can anticipate loadings equal to the ion exchange capacity of the media. In the case of the Purolite A 850 media used here, with ion exchange capacity of 1.25 eq/l, the carrying capacity of the resin is about 0.05 g of CO₂ per gram of resin (Table 1). In slurry form (50% resin) using sea water as the feedwater, this would result in loadings of 25 g CO₂ per liter of feedwater/resin slurry or 12.5 g per liter of feedwater alone. This is well above the value predicted as economic for the Fujairah plant. The economic analysis will be dependent on the amount of fresh water produced from each aliquot of salt water introduced to the system. It appears that the kinetics of the CO₂ release from the ion exchange media are fast. The ratio of CO₂ produced to fresh water produced could therefore be varied to meet the operator's needs. For instance the observed rate of 13 g of water produced for each gram of carbon dioxide is the minimum water production rate – increasing the process time would produce more water at a fixed amount of carbon dioxide.

Conclusions

The concept of combining desalination and carbon dioxide separation appears feasible. The economics are dominated by the water treatment, since large quantities of water need to be produced relative to the amount of carbon dioxide separated (13 to 1 on a mass basis in this study). For circumstances where fresh water is valuable and is being produced from seawater today, it may be feasible to combine the two processes economically. Further study will be required to delineate the economic and engineering aspects of such a combination.

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